

# **Growing season methyl bromide and methyl chloride fluxes at a sub-arctic wetland in Sweden**

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## Abstract

Methyl bromide and methyl chloride fluxes were measured at several sites in a sub-arctic wetland near Abisko, Sweden (68°28'N 18°49'E) throughout the 2008 growing season. Averaged over 92 flux measurements the sub-arctic wetland was found to be a small net sink for CH<sub>3</sub>Br, with mean ( $\pm$  1 sd) uptake of  $-25 (\pm 20) \text{ ng m}^{-2} \text{ h}^{-1}$ , but a small net source of CH<sub>3</sub>Cl with mean emissions of  $400 (\pm 1600) \text{ ng m}^{-2} \text{ h}^{-1}$ . Seasonal trends were observed in both CH<sub>3</sub>Br and CH<sub>3</sub>Cl net fluxes, but diurnal trends for CH<sub>3</sub>Cl only, with peak emissions observed during the afternoon. CH<sub>3</sub>Cl fluxes differed significantly with hydrological status of measurement locations; however, no other substantial correlations were observed between fluxes and external parameters (air and soil temperature and PAR). This study shows that the single previous estimated sink flux for CH<sub>3</sub>Cl in tundra globally (derived from measurements in Alaska) requires revision, although not that for CH<sub>3</sub>Br.

## 1 Introduction

The natural sources and sinks of methyl bromide ( $\text{CH}_3\text{Br}$ ) and methyl chloride ( $\text{CH}_3\text{Cl}$ ) are poorly constrained due to inherent difficulty in obtaining temporally and spatially representative data in heterogeneous natural systems. These gases transport halogen atoms into the upper atmosphere and as emissions of man-made halogen-containing source gases become subject to control, natural fluxes of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  are becoming increasingly important contributors to stratospheric ozone loss processes. It is estimated that by 2100  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  will together contribute approximately 50% of the equivalent effective stratospheric chlorine (EESC) [WMO, 2007], where EESC is a parameter that quantifies the potential for stratospheric ozone depletion for all Cl and Br-containing gases, adjusted to account for the different atmospheric lifetimes of different gases and the substantially greater ozone depletion by Br compared with Cl [Newman *et al.*, 2007; WMO, 2007]. Nearly all natural terrestrial systems thus far investigated have been found to have some role, to greater or lesser extent, on methyl halide fluxes. Consequently, considerable uncertainties remain in constraining terms in the global budgets for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  [WMO, 2003; WMO, 2007].

Temperate wetlands and peatlands are among the established natural sources of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  [Varner *et al.*, 1999; Dimmer *et al.*, 2001]; however global flux estimates for wetlands are based on only a few studies in temperate locations. Wetlands and peatlands are vulnerable to land-use change and potentially to climate change also. High-latitude wetlands, in particular, are already being affected by warmer temperatures with reduced permafrost observed in some locations [ACIA, 2005].

Although high-latitude wetlands are not anticipated to be a major source or sink of CH<sub>3</sub>Br or CH<sub>3</sub>Cl, it is important that CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes from these areas are quantified in order to constrain CH<sub>3</sub>Br and CH<sub>3</sub>Cl budgets and to make predictions about future flux patterns in a changed climate. Data for CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes at polar latitudes have been reported previously only for arctic Alaskan tundra [Rhew *et al.*, 2007; Teh *et al.*, 2009], and did not include measurements over the full growing season.

Seasonal and diurnal trends in CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes from non-polar ecosystems have been reported in a number of studies [*e.g.* Redeker *et al.*, 2000; Rhew *et al.*, 2002; White *et al.*, 2005; Drewer *et al.*, 2006; Manley *et al.*, 2006], but there has been no consistent evidence for external parameters driving CH<sub>3</sub>Br or CH<sub>3</sub>Cl fluxes across all ecosystem types; individual studies have suggested that light [Drewer *et al.*, 2006], temperature [Rhew *et al.*, 2000; Rhew *et al.*, 2002; Redeker and Cicerone, 2004], or soil pore-water saturation [Redeker and Cicerone, 2004] may affect emissions. In arctic Alaskan tundra it was found that drained sites had greater rates of CH<sub>3</sub>Br and CH<sub>3</sub>Cl uptake than flooded sites in both coastal and inland areas [Rhew *et al.*, 2007; Teh *et al.*, 2009], with water table depth correlating most strongly with CH<sub>3</sub>Cl and CH<sub>3</sub>Br net uptake [Teh *et al.*, 2009].

In this study, CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes were measured at a number of sites in sub-arctic wetland near Abisko, Sweden throughout the 2008 growing season (June – September), including a number of intra-daily flux measurements. Data for external parameters including air temperature, ground temperature, chamber temperature and photosynthetically active radiation (PAR) were also collected.

## 2 Experimental

### 2.1 Sampling sites

Flux measurements were undertaken in sub-arctic wetland areas in the vicinity of the Abisko Scientific Research Station (ANS), Abisko, northern Sweden (68°28'N 18°49'E). An initial study was carried out in August 2007 (for CH<sub>3</sub>Br only) and a longer, seasonal study was carried out from June to September 2008 to capture the sub-arctic growing season.

In the initial set of measurements, in August 2007, air samples were collected from 15 sampling points situated within 5 different wetland locations. Four locations were 1.5 km south of ANS, at elevations between 420 and 440 m a.s.l. (average precipitation 304 mm p.a), whilst the fifth location was Stordalen Mire, 10 km east of ANS, at 360 m a.s.l. (average precipitation 400 mm p.a.). The sun was above the horizon between 18.5 and 20 hours per day during the two week sampling period and there was no complete darkness. The individual sampling points within a location were chosen to capture the differences in hydrology and vegetation at that location. Broadly these could be divided into wet areas, dry areas and damp areas. A summary of the major types of vegetation present in each category is given in Table 1.

Regular two-weekly measurements were made throughout the full 2008 sub-arctic growing season (June – September 2008) at two of the locations 1.5 km south of ANS used in the initial study. There were six sampling sites in total, two each in areas designated as wet, damp and dry. The hours of daylight varied over the study period. Until 23 July the sun never set, thereafter declining to 15 h per day above the horizon by 4 September. However, even under

clear-sky conditions sampling sites were not necessarily exposed to direct sunlight because of shadowing from surrounding mountains.

## 2.2 Sampling methods

At each sampling point a 400 mm diameter by 200 mm high PVC collar was sunk 150 mm into the ground and remained in place for the duration of the sampling campaign. To collect a flux sample an appropriately sized chamber was secured to the collar to create an airtight enclosure. In the initial study, either a 0.044 m<sup>3</sup> chamber or a Perspex sheet was used depending on the height of the vegetation within the collar. For the seasonal study, a 0.031 m<sup>3</sup> chamber was used. Chambers were sealed for 10 min after which a 500 mL sample was withdrawn by gas-tight syringe and transferred to an evacuated 1 L Tedlar bag. An ambient air sample was similarly collected. Bags were couriered to the University of Edinburgh for analysis. The ambient air temperature, sub-surface temperature at 5 cm depth and the internal chamber temperature, were recorded at each sampling event. Continuous measurements of PAR were available from the ANS weather station.

## 2.3 Analysis methods

The air samples were analysed for CH<sub>3</sub>Br and CH<sub>3</sub>Cl using an HP5890 gas chromatograph equipped with electron capture detection and a ZB642 capillary column (Phenomenex Inc., Torrance, CA, USA) 30 m in length, i.d. 0.32 mm and 1.8 µm film thickness. A custom built, two-stage preconcentration unit was used prior to GC separation [Drewer *et al.*, 2008]. The first trap was a ¼ inch diameter by 100 mm long stainless steel tube filled with Tenax TA 60/80 mesh (Supelco, Bellefont, PA, USA). This was cooled to -30°C before sample loading

using dual two-stage Peltier cells (Melcor, Trenton, NJ, USA). The second trap was a 1/8 inch diameter by 200 mm long stainless steel tube filled with fine glass beads and cooled to  $-80^{\circ}\text{C}$  using dry ice. A 100 mL sample aliquot was loaded onto the first trap and the trapped analytes subsequently transferred to the second trap using switching valves (VICI, Houston, TX, USA). After 5 min the second trap was flash heated to transfer the analytes onto the column. The temperature programme was 5 min at  $40^{\circ}\text{C}$ , ramping for 5 min at  $40^{\circ}\text{C min}^{-1}$  and hold for 5 min at  $240^{\circ}\text{C}$ .

Calibration curves for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  were prepared weekly using dilutions of certified standards:  $500 \pm 10$  ppbv  $\text{CH}_3\text{Br}$  in nitrogen (Air Products Inc.) and  $15.8 \pm 0.5$  ppmv  $\text{CH}_3\text{Cl}$  (Air Liquide). Since a net flux is derived from difference between parallel enclosure and ambient samples, some sources of uncertainty subtract out, for example in primary standard concentrations and their dilutions in an individual calibration curve. The major uncertainty in an individual net flux value arises from the interpolations from a given calibration regression fit. This uncertainty was propagated with uncertainties in other relevant parameters, e.g. enclosure net volume, to derive an estimate of overall standard deviation in net flux value. Double these  $\pm 1 \sigma$  values were used to define the limits of detection for net flux from the field chambers, yielding values of  $\pm 21$  and  $\pm 490 \text{ ng m}^{-2} \text{ h}^{-1}$ , for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , respectively.

### 3 Results

Figure 1 shows the time series of net  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  fluxes during the 2008 growing season for those measurements made within the time period 10:00 – 16:30 on each occasion. These data constitute the first full-season time series of methyl halide fluxes at high latitude. Seasonal variation is apparent for both  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , with flux magnitudes changing

most markedly through June and early July, corresponding to the most active period of the growing season, and smallest net fluxes at the beginning and end of the growing season.

Figure 2 shows the net CH<sub>3</sub>Br and CH<sub>3</sub>Cl fluxes measured at four-hourly intervals over a 24 h period on 4<sup>th</sup> June from collars ‘Wet 2’, ‘Dry 2 and ‘Damp 1’. CH<sub>3</sub>Br fluxes were very small during this sampling period and there was no significant diurnal flux trend for any of the three sites. In contrast, there was some diurnal variation in CH<sub>3</sub>Cl fluxes, with a peak occurring around the middle of the day for all three sites investigated. Air temperature varied from a low of 8.9°C (averaged across sites) at 00:30 am to a high of 20.5°C at 16:30 pm and soil temperatures followed a similar cycle. The lag between peak temperature and peak CH<sub>3</sub>Cl emissions is consistent with the paradigm of uptake and emission processes occurring simultaneously (see section 4). Peak emissions related to plant activity occur when there is most light, around midday, but as soil temperatures increase, bacterially-mediated uptake processes increase, reducing the net flux to the atmosphere.

Aside from the diurnal cycle in net CH<sub>3</sub>Cl flux noted above, no substantial correlations between CH<sub>3</sub>Br or CH<sub>3</sub>Cl flux and air temperature, chamber temperature, sub-surface temperature or PAR were discernible for the time series data in this study. It is inherently difficult to tease out any such relationship(s), if they exist, from *in situ* field data due to uncontrolled confounding between these factors (e.g. temperature and PAR) and with other factors (e.g. date during season and individual site characteristics).

However, the magnitude of CH<sub>3</sub>Cl fluxes did differ significantly (ANOVA) between locations classified according to their hydrology and vegetation (Figure 3). Mean ( $\pm$  1 sd) CH<sub>3</sub>Cl fluxes from each of the pairs of locations designated ‘Wet’, ‘Damp’ and ‘Dry’ were -160 ng m<sup>-2</sup> h<sup>-1</sup>,



1300 ng m<sup>-2</sup> h<sup>-1</sup> and 620 ng m<sup>-2</sup> h<sup>-1</sup>, respectively. These averaged values mask an important observation from Figure 1b that locations classified as ‘Dry’ had the greatest seasonal range in fluxes, having generally greater net emission of CH<sub>3</sub>Cl than other sites in the early part of the season, but greater net uptake of CH<sub>3</sub>Cl in the latter part of the season. CH<sub>3</sub>Br fluxes did not differ significantly with hydrology/vegetation classification, although there was a non-significant tendency for greater CH<sub>3</sub>Br uptake at drier sites (Fig. 1a).

## 4 Discussion

A seasonal variation in net CH<sub>3</sub>Br or CH<sub>3</sub>Cl fluxes, as observed here, was not reported by Rhew *et al.* [2007] for their coastal Alaskan arctic tundra site, but their measurements only spanned the period late June to August.

The sampling sites at Abisko were generally a net sink for CH<sub>3</sub>Br. The mean ( $\pm 1$  sd) net CH<sub>3</sub>Br flux for the data shown in Figure 1 is -30 ( $\pm 25$ ) ng m<sup>-2</sup> h<sup>-1</sup> ( $n = 60$ ), with greatest net uptake coincident with the longest days in late June and early July. Including all flux measurements made during daylight hours between June and September at these sites yields an overall mean ( $\pm 1$  sd) net CH<sub>3</sub>Br flux of -25 ( $\pm 20$ ) ng m<sup>-2</sup> h<sup>-1</sup> ( $n = 92$ ). The similar mean fluxes for the full and subset of measurements is consistent with the interpretation that any diurnal variability is insignificant compared with variability on the week-to-week time scale and between sites. The small net uptake of CH<sub>3</sub>Br observed at these high-latitude wetlands contrasts with the net emissions measured at wetland and peatland areas in Scotland (Hardacre, unpublished data), Ireland [Dimmer *et al.*, 2001] and New Hampshire, USA [Varner *et al.*, 1999] but is consistent with the net CH<sub>3</sub>Br uptake reported for arctic Alaskan tundra [Rhew *et al.*, 2007; Teh *et al.*, 2009]. These latter studies reported average net CH<sub>3</sub>Br

flux of  $-18 \pm 22$  ( $n = 40$ ) and  $-45 \pm 60$  ( $n = 36$ )  $\text{ng m}^{-2} \text{h}^{-1}$  (converting these authors' standard errors to standard deviations for comparison with presentation here).

During the initial study at Abisko in August 2007, the mean ( $\pm 1$  sd) net  $\text{CH}_3\text{Br}$  flux was  $-17$  ( $\pm 17$ )  $\text{ng m}^{-2} \text{h}^{-1}$  ( $n = 16$ , data not shown). Comparing this with the average flux in August 2008 of  $-13$  ( $\pm 19$ )  $\text{ng m}^{-2} \text{h}^{-1}$  ( $n = 16$ ) shows there was no substantive inter-annual variation in  $\text{CH}_3\text{Br}$  flux between these two years. In the Alaskan studies, the greater net uptakes of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  observed in 2006 than in 2005 was attributed to the higher soil temperatures in 2006 [Rhew *et al.*, 2007; Teh *et al.*, 2009].

The seasonal pattern of  $\text{CH}_3\text{Cl}$  net fluxes at the Abisko sites was different to that of  $\text{CH}_3\text{Br}$  (Fig. 1). Net emission of  $\text{CH}_3\text{Cl}$  was generally observed during the period early June to late July (except at collar 'Dry 2'), with more net uptake later in the season. Measurements on 11 Aug showed comparatively large uptake of  $\text{CH}_3\text{Cl}$  at all sites. There was no obvious reason to doubt the authenticity of these data. On average, net flux was positive: mean ( $\pm 1$  sd) net  $\text{CH}_3\text{Cl}$  flux for the data shown in Figure 1 was  $550$  ( $\pm 1800$ )  $\text{ng m}^{-2} \text{h}^{-1}$  ( $n = 60$ ), or  $400$  ( $\pm 1600$ )  $\text{ng m}^{-2} \text{h}^{-1}$  if all 92 measurements made during daylight hours are included. Again the comparable mean values demonstrate that seasonal and spatial differences dominate the flux variability. Likewise, the larger relative standard deviation in the  $\text{CH}_3\text{Cl}$  flux measurements compared with the  $\text{CH}_3\text{Br}$  flux measurements reflects the larger seasonal variation in the former than in the latter. The small net emission observed for  $\text{CH}_3\text{Cl}$  on average across 6 sites and the whole growing season at Abisko is consistent with observations of emissions, on average, in Scottish wetlands (Hardacre, unpublished data) and Irish peatlands [Dimmer *et al.*, 2001] but in contrast to the average net  $\text{CH}_3\text{Cl}$  uptakes of  $637$  ( $\pm 610$ )  $\text{ng m}^{-2} \text{h}^{-1}$  [Rhew *et*

*al.*, 2007] and  $1240 (\pm 1350) \text{ ng m}^{-2} \text{ h}^{-1}$  [Teh *et al.*, 2009] reported for the Alaskan tundra sites (again converting these authors' expressions of variability into standard deviations).

An association between hydrology and methyl halide fluxes has been reported previously. Both Rhew *et al.* [2007] and Teh *et al.* [2009] measured greater  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  uptake at drier locations in their studies in Alaskan tundra, with the latter reporting that water table depth was the best predictor of both net and gross  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  uptake. On the other hand, Redeker and Cicerone [2004] reported that low water conditions in rice paddies, another highly moist environment, enhanced net  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  emission from certain rice cultivars. The current field study does not distinguish whether the difference in  $\text{CH}_3\text{Cl}$  (and  $\text{CH}_3\text{Br}$ ) fluxes between sites was driven by the vegetation or the hydrological status, but it is likely that both are relevant as there was not a consistent trend in  $\text{CH}_3\text{Cl}$  flux from wet to dry soil conditions.

The picture that emerges from consideration of this study in Swedish high-latitude wetlands, and the studies in arctic Alaska [Rhew *et al.*, 2007; Teh *et al.*, 2009] and New Hampshire peatlands [White *et al.*, 2005] (together with further data from wetlands and peatlands in Scotland) is of land-atmosphere  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  fluxes in such systems being the net resultant of plant- and soil-mediated emission and soil-mediated uptake; and that the relative magnitudes of each varies with micro-topology of the site (i.e. with vegetation and hydrology) and with time during the season. The latter factor impacts on vegetation activity and hydrology. Soils at the start of the season at Abisko are wetter than subsequently due to snow and ground-ice melt, so soil uptake rates are lower, yet plant-related activity is higher. The net flux is dynamically sensitive to changes in soil moisture and biological activity as the season progresses through to drier but cooler conditions and decreased vegetation growth. This

picture is consistent with the observation by Teh *et al.* [2009] that the limitation on methyl halide uptake in saturated soils is due to mass transfer limitation rather than reduced microbial activity under anaerobic conditions. It also consistent with the suggestion that measurements of CH<sub>3</sub>Cl fluxes which miss the beginning of the growing season in these ecosystems will likely show averaged net negative flux overall.

When comparing the results from this study site with those in Alaska [Rhew *et al.*, 2007; Teh *et al.*, 2009], it is also important to remember that the Abisko sites, although within the Arctic Circle, differ from the Alaskan sites not only biogeographically but in being classified as sub-arctic in terms of vegetation cover and climate rather than arctic. The warmer sub-arctic climate, and generally greater vegetation cover, appears to result in small net CH<sub>3</sub>Cl emissions prevailing at Abisko when integrated over the full growing season and all sites, consistent with observations of net CH<sub>3</sub>Cl emissions overall in other comparatively high-latitude wetlands in Ireland [Dimmer *et al.*, 2001] and Scotland (Hardacre, unpublished).

## **5 Global implications**

Rhew *et al.* [2007] estimated net annual uptake rates of 0.3 Gg CH<sub>3</sub>Br and 11.2 Gg CH<sub>3</sub>Cl for tundra worldwide assuming a total tundra surface area of  $7.3 \times 10^{12} \text{ m}^2$  and that their average net fluxes of  $-18 \text{ ng CH}_3\text{Br m}^{-2} \text{ h}^{-1}$  and  $-637 \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$  applied over a 100-day growing season to all such ecosystems globally. The CH<sub>3</sub>Br flux data from this study suggest that this CH<sub>3</sub>Br estimate does not need to be revised. However, the small net CH<sub>3</sub>Cl emission observed in this work suggests that the previous extrapolated global net uptake estimate for CH<sub>3</sub>Cl may need to be revised downward to take account of these data for the Swedish arctic.

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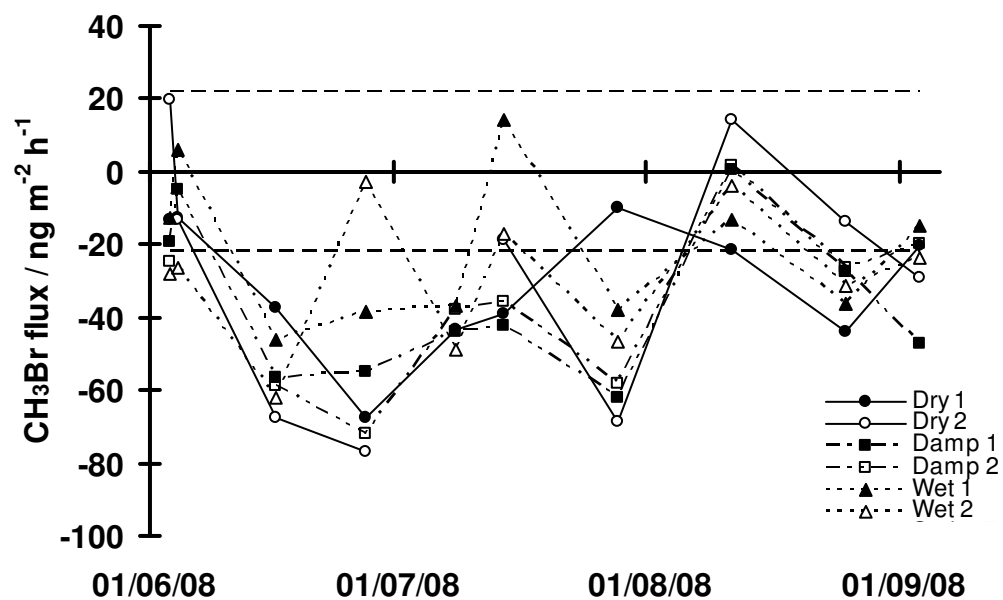
**Table 1:** Classification of sampling sites according to hydrological condition and main types of vegetation present.

Water conditions	Main plant species present
Wet	<i>Carex rostrata</i> , bryophytes
Damp	<i>Equisetum palustre</i> , sphagnum mosses
Dry	<i>Vaccinium spp.</i> , <i>Betula nana</i> , <i>Empetrum nigrum</i> , <i>Andromeda polifolia</i> , <i>Eriophorum spp.</i> , <i>Rubus chamaemorus</i> , lichens, bryophytes

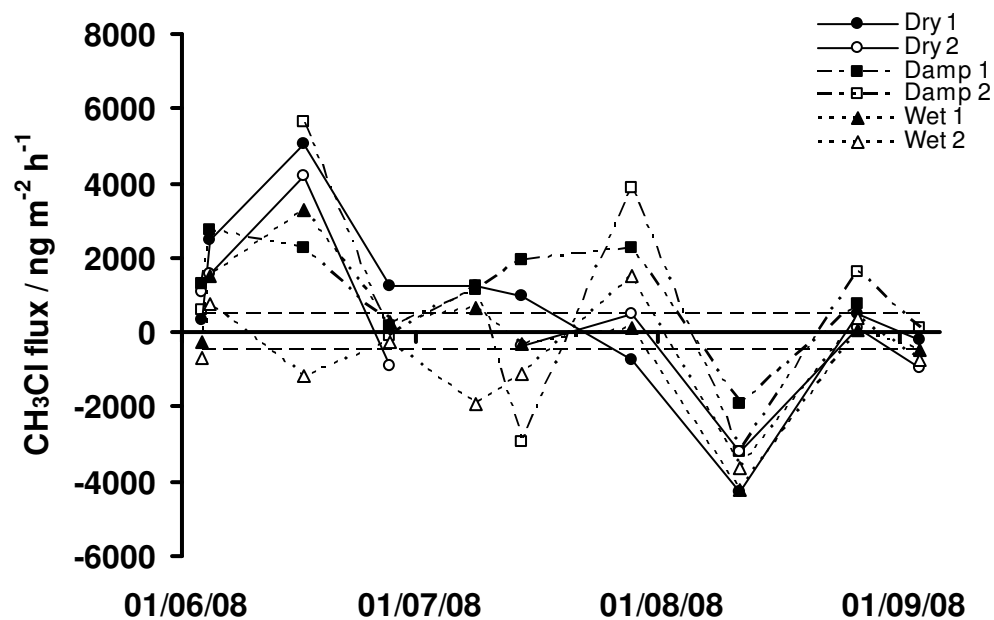


**Figure 1:** Time series of (a) net  $\text{CH}_3\text{Br}$  flux and (b)  $\text{CH}_3\text{Cl}$  flux from six sites during the 2008 growing season. Horizontal dashed lines indicate limits of detection for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  net flux determination..

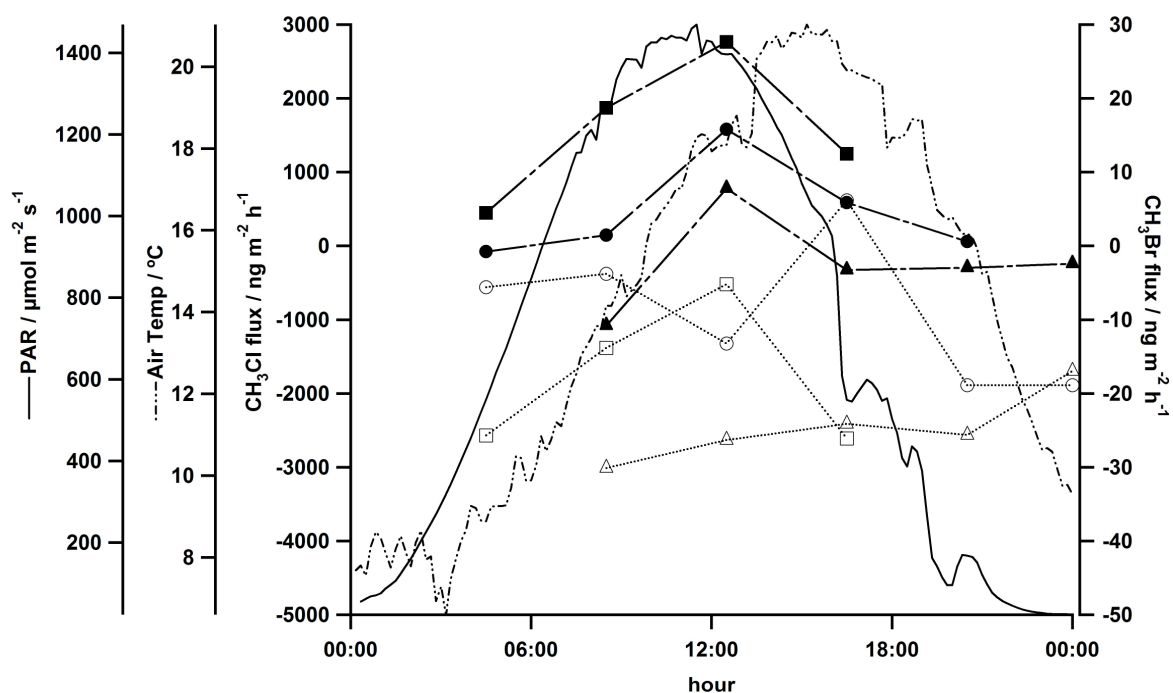
(a)



(b)



**Figure 2:** CH<sub>3</sub>Br (open symbols) and CH<sub>3</sub>Cl (solid symbols) fluxes from sites ‘Wet 2’ (circles), ‘Dry 1’ (squares) and ‘Damp 1’ (triangles), together with ambient air temperature and PAR, measured over a 24 hour period on 4 June 2008. Limits of detection for net flux determination are  $\pm 21 \text{ ng m}^{-2} \text{ h}^{-1}$  and  $\pm 490 \text{ ng m}^{-2} \text{ h}^{-1}$  for CH<sub>3</sub>Br and CH<sub>3</sub>Cl, respectively.



**Figure 3:** Average  $\text{CH}_3\text{Cl}$  fluxes during the seasonal study as a function of location hydrological classification. Error bars illustrate the magnitude of the limit of detection ( $\pm 490 \text{ ng m}^{-2} \text{ h}^{-1}$ ) for an individual net  $\text{CH}_3\text{Cl}$  flux measurement.

